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Final

Bunker Hill Mine Water Treatability Study Work Plan

Bunker Hill Mine
Kellogg, Idaho

Prepared for

U.S. EPA, Region 10

July 1999

CH2MHILL

EPA Contract No. 68-W-98-228
Work Assignment No. 021-RI-CO-105G

CH2M HILL Project No. 152215.TT.06

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SECTION 1
Introduction

This treatability study work plan has been prepared by CH2M HILL for the U.S. Environmental Protection Agency (EPA), Region 10, Under Work Assignment No. 021-RI-CO-105G. The purpose of this work plan is to describe the treatability testing to be conducted in support of the Presumptive Remedy process being undertaken to develop a long-term, cost-effective management system for the Bunker Hill Mine acid mine drainage (AMD). This work plan which has been prepared in accordance with EPA's guidance for conducting treatability studies under CERCLA, contains the following sections:

Section 1: Introduction
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1.1 Background

Seven process alternatives were identified in the *Bunker Hill Mine Water Presumptive Remedy* (Draft Technical Memorandum prepared by CH2M HILL for EPA Region 10, January 22, 1999) as possible supplemental processes that might be added onto a new high density sludge (HDS) treatment plant at the Bunker Hill Mine site. Three of these alternatives included two sub-options, consisting of either granular media filtration or micro-filtration. The three process options recommended for treatability testing are as follows:

Alternative 5 – HDS + **Media Filtration + Sulfide-functional ion exchange**

Alternative 3 – HDS + **Iron co-precipitation + Micro-filtration or Media filtration**

Alternative 4 – HDS + **Insoluble sulfide precipitation + Micro-filtration or Media filtration**

The following subsections provide the rationale for selecting these particular technologies.

1.1.1 Sulfide-Functional Ion Exchange

Alternative 5, HDS + Media filtration + Sulfide-functional ion exchange has the potential for meeting the draft treatment requirements (Section 1.2) and has several favorable features:

- In the ion exchange process, metal is adsorbed onto the solid substrate of the resin beads, thereby avoiding the need for sulfide chemical addition and a subsequent solid/liquid separation step such as media- or micro-filtration following the process (although pre-filtration may be required). Sulfide precipitation processes may precipitate the metal sulfide as a colloidal solid that is difficult to filter.
- The application of sulfide as a regenerable solid avoids the potential of reagent (for example, soluble sulfide) overdosing, which can re-dissolve the metal (in some cases) or may cause formation of a stabilized colloid that is difficult to remove.
- Sulfide-functional resins have a very high selectivity for certain heavy metals—specifically those that form insoluble sulfides. The high selectivity makes it possible to adsorb metals from very dilute solutions without competition from the more common metals such as aluminum, calcium, magnesium, potassium, and sodium.

There are some potential disadvantages to the process, however. Among these are use of regenerant solutions to remove the accumulated metals from the resin (which increases the dissolved solids concentration in plant effluent); and possible difficulties in removing some of the metals from the used resin (thereby necessitating resin replacement instead of regeneration and reuse).

1.1.2 Iron Co-Precipitation

Alternative 3, HDS + Iron co-precipitation + Micro-filtration or Media filtration, also has the potential of meeting the draft treatment requirements. Favorable features of this option include:

- Micro-filtration will remove solid material into the colloidal size range, which might otherwise cause metal discharges in excess of the target mass loading. Media filtration will remove somewhat less solid material.
- The treatment reagent is readily available and creates a by-product sludge that is probably non-hazardous, and closely resembles process sludge from the existing HDS plant.
- There is some operating history and experience with the iron co-precipitation process in industrial applications.

Iron co-precipitation could be conducted within the HDS neutralization reactor or in a separate reactor following HDS clarification.

The primary limitations of the iron co-precipitation process are:

- Most commercially available iron salts contain impurities that could <u>increase</u> the metal concentrations in treated water, if the iron dosage were too high.

- The metal removal efficiency is not as high as for sulfide-based processes because the "binding strengths" of the metals with iron hydroxide floc are not as strong as between the metals and sulfide.

1.1.3 Insoluble Sulfide Precipitation

Alternative 4, HDS + Insoluble sulfide precipitation + Micro-filtration or Media filtration, also has the potential of meeting the draft treatment requirements. The most favorable feature of this option is that there is some operating history and experience with insoluble sulfide post-treatment in industrial applications.

The main drawback of this process is that there is a relatively low utilization efficiency of the reagents that are used in the process. In addition, the insoluble sulfide process is more complicated than the iron co-precipitation process, and consequently is more difficult to optimize. Sulfide precipitation could be conducted within the HDS neutralization reactor or in a separate reactor following HDS clarification.

1.2 Treatment Goals

Draft TMDL waste load allocations at different receiving stream flows are listed in Table 1-1 for zinc, lead, and cadmium. The equivalent concentrations based on a historical average Central Treatment Plant (CTP) effluent flow rate of 2,240 gallons per minute (gpm) are also shown in Table 1-1. Using this concentration-based approach to estimating the future CTP limits, the draft discharge limits will be from one to three orders of magnitude lower than the current discharge requirements for the CTP, depending on the flow in the river. For example, the Draft Total Maximum Daily Load (TMDL) for total zinc is 44.1 micrograms per liter (μg/L) (50 percent river flow) as opposed to the current daily maximum limit of 1,480 μg/L. The equivalent concentrations shown in Table 1-1 derived from the draft mass-based TMDLs are assumed to represent treatment goals for this treatability study, although the future discharge limits for Bunker Hill Mine have not been finalized.

1.3 Phased Treatability Study Approach

This treatability study work plan describes the test approach and procedures for evaluating treatment of Bunker Hill Mine water by iron co-precipitation, sulfide precipitation, and sulfide functional ion exchange. A phased testing approach will be followed:

Phase 1—Bench-scale screening designed to obtain information about treatment performance potential and identify, for further consideration, technologies that exhibit the potential for meeting treatment goals.

Phase 2—Testing designed to obtain quantitative performance data on one or more technologies/alternatives retained from Phase 1. This phase may include additional bench-testing and/or pilot-scale testing.

Phase 3—Optional testing that may be needed to obtain technology-specific, detailed design information.

TABLE 1-1
Draft TMDL Waste Load Allocations (WLA)
Limits are based on total recoverable metal

	7Q10[b] River Flow		10% River Flow		50% River Flow		90% River Flow		River Water Quality Criterion
Parameter	**µg/L[a]**	**lb/day**	**µg/L[a]**	**lb/day**	**µg/L[a]**	**lb/day**	**µg/L[a]**	**lb/day**	**µg/L**
Total zinc	11.5	0.309	13.7	0.370	52	1.40	183	4.92	32
Total lead	0.48	0.0130	0.58	0.0156	2.18	0.0589	7.7	0.207	0.54
Total cadmium	0.157	0.00423	0.188	0.00506	0.711	0.0192	2.5	0.0674	0.38

[a] Concentration limits are based on a historical CTP effluent flow rate of 2,240 gpm. The mass-based limits are based on river flow and not effluent flow; at a given river flow condition, the allowable effluent concentration will be higher if effluent flow is decreased; and lower if the effluent flow is increased.

[b] The 7Q10 river flow is the lowest 7-day average daily river flow that occurs with a 10-year return period. This flow is the characteristic flow used for water quality compliance for chronic aquatic health criteria, as required by the National Toxics Rule.

This work plan provides detailed procedural information for Phase 1 only. Phase 1 will consist of batch isotherm testing of sulfide functional ion exchange, and batch jar testing of iron co-precipitation and sulfide precipitation. Possible objectives for Phase 2 are given but the testing details will depend on the results of Phase 1 and, therefore, cannot be accurately specified at this time.

The three treatment technologies under evaluation would be applied in conjunction with hydroxide precipitation by the HDS process. Although it is possible to incorporate the two precipitation processes into the HDS process system, it is believed that the best treatment can be achieved in a post-HDS treatment scenario. Consequently, testing is designed to simulate post-HDS treatment by using effluent from the existing CTP. Enhanced co-precipitation within the HDS system using iron or sulfide may be tested in Phase 2 if warranted based on the Phase 1 post-HDS treatment test results.

Because Phase 1 is intended to evaluate the *potential* effectiveness achievable by the technologies, treatment performance will be evaluated based on the removal of *soluble* metals. The rationale is that the degree of removal of non-soluble (that is, particulate) metals is a function of the solids/liquid separation technique employed and that engineered solutions are available for improving particulate removal (for example, in order of increasing solids removal efficiency, sedimentation, sand filtration, multi-media filtration, micro-filtration). While it is not necessary to evaluate the different filtration sub-options in Phase 1 to assess treatment performance potential, it may be appropriate to test them during Phases 2 and/or 3.

SECTION 2

Test Objectives

The overall goal of the entire treatability study program is to develop information needed to reduce metals concentrations in Bunker Hill Mine discharge to levels compatible with treatment goals.

The specific objectives of Phase 1 testing are the following:

- Proof of principle—that is, to determine if the alternative is potentially able to meet treatment goals
- Preliminary chemical dose optimization (for iron co-precipitation)
- Preliminary pH optimization (for iron co-precipitation and sulfide precipitation)
- Comparison of treatment effectiveness for target metals achieved by iron co-precipitation and sulfide precipitation
- Development of isotherm data for two types of sulfide functional group ion exchange resins (Thiol and Thiouronium)
- Evaluation of regenerability of the ion exchange resins
- Identification of the best resin type for removal of target metals for further testing

Possible objectives for Phase 2 testing may include the following:

- Further optimization of chemical doses and operating pH
- Evaluation of the effects of retention time, oxidation, temperature, and wastewater variations on treatment performance
- Assessment of granular media filtration and micro-filtration process effectiveness and effects of polymer addition
- Determination of ion exchange resin loading capacity, breakthrough characteristics, regeneration efficiency, and service life
- Evaluation of treatment process reliability
- Preliminary equipment sizing and estimates of capital and operating cost ranges
- Evaluation of the effectiveness of the selected technologies on other parameters of concern
- Evaluation of settling performance
- Evaluation of residuals characteristics and impact of recycle streams on the HDS process

SECTION 3

Experimental Design and Procedures

This section describes the experimental design and procedures for Phase 1 testing. These procedures have been selected to meet the test objectives based on the information available at the time of plan preparation. New information may become available during the course of the testing program, which may necessitate changes to test procedures or protocol in order to meet the test objectives. If so, these changes will be reviewed with EPA prior to being implemented.

3.1 Sample Collection and Characterization

Synoptic (representing approximately the same wastewater conditions) samples of raw AMD (Kellogg Tunnel discharge), CTP influent, and CTP effluent will be collected for characterization analysis and/or treatability testing. Anticipated volume requirements are 1 gallon of raw AMD, 1 gallon of CTP influent, and 30 gallons of CTP effluent. Samples can be collected in 1-gallon plastic cubitainers and a 30-gallon plastic drum. Sampling procedures are described in Section 4. Samples will be shipped to CH2M HILL's Applied Sciences Laboratory in Corvallis, Oregon, where Phase 1 treatability testing will be performed. This location was selected for several reasons, including the following:

- The availability of lab space, treatability test equipment, high-purity chemicals, and utilities, such as Milli-Q water. This will enhance QA/QC and reduce the potential for propagation of error due to external environmental factors, such as that which might occur if the Phase 1 testing were performed in the field.
- The availability of rapid turnaround for chemical analyses, when and if required.
- The presence of qualified chemists and treatability personnel, which will enhance testing QA/QC and avoid the need for personnel to travel to the site (thereby reducing the cost).

Characterization analyses will be performed on the raw AMD, CTP influent, and CTP effluent samples. Unpreserved CTP effluent samples will be analyzed "as-received" at the Corvallis lab and separate aliquots of the CTP effluent sample will be collected and preserved in the field at the time of sample collection and analyzed for selected characterization parameters. The resulting two data sets will be compared to evaluate the extent of changes that occur during sample shipping (for example, conversion between dissolved and particulate metal forms). In addition, the CTP effluent received at the lab will be analyzed after adjusting the pH to various levels with lime, to evaluate changes in dissolved metals concentrations if the HDS treatment system were operated at different pH levels. The lime additions will be conducted in a series of beakers using a conventional jar-stirring apparatus (Table 3-1). The raw AMD sample will be analyzed as-received to document raw wastewater characteristics entering the CTP at the time of sampling. CTP operating conditions during sample collection will also be recorded.

TABLE 3-1
CTP Effluent Sample Pre-treatment

Sample	Jar Number	Target pH
CTP Effluent	P1.1	No adjustment*
CTP Effluent	P1.2	9.5
CTP Effluent	P1.3	10
CTP Effluent	P1.4	10.5
CTP Effluent	P1.5	11.0

* Assumed ~ pH 9.0; if not, add Jar P1.12 and use a target pH of 9.0.

The CTP currently is configured and operates in the HDS mode, but uses a minimum of sludge recycle, which reduces the terminal percent solids of the wasted sludge. In the future, the CTP will be upgraded and operated at a higher solids recycle ratio, which will increase the terminal sludge percent solids. The dissolved species present in the CTP effluent are primarily a function of pH and should not be significantly different in the current mode of operation in comparison to the future mode of operation. Thus, for the purposes of the Phase 1 testing, the current CTP effluent will be used. In future phases, the treatability testing may include simulation of the HDS process.

The raw AMD, CTP influent, and as-received CTP effluent samples will be analyzed for total and dissolved Target Analyte List (TAL) metals, silver (Ag), aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thallium (Tl), vanadium (V), zinc (Zn); pH; alkalinity (as received CTP effluent only); sulfate; total suspended solids (TSS); and total dissolved solids (TDS). The raw AMD and CTP influent will also be analyzed for lime demand and solids formed. The field CTP effluent samples will be analyzed for pH and total and dissolved cadmium, lead, zinc, iron, and manganese. The pH-adjusted CTP effluent samples will be filtered through a 0.2-μm Teflon membrane filter and analyzed for dissolved cadmium, lead, zinc, iron, and manganese.

Results from the pH-adjustment tests will be used to determine whether the current target pH of 9.0 is the best pH level for the HDS process. If another pH provides further reductions in dissolved cadmium, lead, and zinc, pH-adjusted HDS effluent may be used in subsequent treatment testing.

3.2 Iron Co-Precipitation Testing

This testing will evaluate the effectiveness of soluble metals removal from HDS process effluent by iron co-precipitation. In the iron co-precipitation process, a soluble iron salt is added to the wastewater to form an iron oxyhydroxide precipitate, and removal of dissolved metals occurs via incorporation into the iron precipitate matrix and adsorption onto the iron floc surface. Iron salt choices include ferric chloride, ferric sulfate, and ferrous sulfate. Ferric sulfate [$Fe_2(SO_4)_3$] will be used for proof-of-principle Phase 1 testing. It is believed that the form of the ferric salt used should not significantly impact performance. Testing will be performed on effluent from the HDS process thickener or pH-adjusted HDS effluent, based on the Subsection 3.1 test results (referred to as the "test water").

3.2.1 Equipment and Supplies

Two six-paddle, adjustable-speed, jar stirrers with polyethylene paddles will be used for conducting batch precipitation tests. Other equipment and supplies include twenty 1.5-liter polyethylene beakers, automatic pipets with disposable plastic tips, pH meter, oxidation-reduction potential (ORP) meter, timer, vacuum filtering apparatus and a supply of 0.2- and 0.45-µm Teflon membrane filters, balance, magnetic stirrer with stirbars, specialty pre-cleaned and pre-analyzed polyethylene or polypropylene sample bottles, and a high-purity lab water supply (Milli-Q water). All plasticware and glassware (other than the pre-cleaned sample bottles) will be thoroughly cleaned (acid washed, Milli-Q water rinsed) prior to each use.

3.2.2 Reagents

- Ferric sulfate solution—approximately 10 mg Fe/mL. Stock solution makeup: add 17.9 g reagent grade $Fe_2(SO_4)_3$-xH_2O to a 500-milliliter (mL) volumetric flask and bring to volume with Milli-Q water. Also make a ca. 1 mg Fe/mL solution by diluting this 1:10.
- Lime slurry—approximately 10 mg/mL. Stock solution makeup: add 10 grams reagent-grade $Ca(OH)_2$ to 1 liter of Milli-Q water. Stir slurry continuously on magnetic stirrer during use. Make up a new batch of lime slurry each day of testing.
- Sulfuric acid solution for pH adjustment—6 N. Stock solution makeup: add 167 mL of reagent-grade concentrated H_2SO_4 to a 1-liter volumetric flask and bring to volume with Milli-Q water.

Stock solution concentrations may be varied, as needed, to allow convenient pH adjustment.

3.2.3 Procedure

Standard jar test procedures will be used in an iterative approach to optimize pH and then optimize the iron dose. The jar test procedure is described below.

Test Series 1—pH optimization

1. Add 1 liter of test water to each of 10 beakers numbered as shown in Table 3-2 and add 1 liter of Milli-Q water to the 11th beaker (method blank). Place beakers on jar stirrers and record the starting pH and oxidation-reduction potential (ORP). If the sample ORP is substantially different from (lower than) that measured in CTP effluent in the field, aeration of the samples will be considered.
2. Add iron stock solution to jars F2.1 -F2.10 to produce a concentration of 10 mg/L of iron, while rapid mixing at 100 revolutions per minute (rpm). This dose was somewhat arbitrarily selected as a reasonable starting point based on a review of the literature and our experience (there is no stoichiometry, per se, associated with the iron co-precipitation process). Record pH after iron addition and volume of reagent added.

3. Add lime slurry or sulfuric acid solution to the jars to produce the pH levels indicated in Table 3-2. Make sure the pH levels stabilize. Record the volume of pH-adjustment reagent added to each jar.
4. Rapid mix for 1.5 minutes.
5. Slow mix at 15 to 20 rpm for 20 minutes. Adjust paddle speed, if necessary, to promote flocculation and prevent floc sheer.
6. Turn off the mixer and remove paddles from jars; allow samples to settle for 30 minutes (a longer settling time is acceptable if it facilitates filtration). Record observations on floc and settling characteristics and sludge quantity. Measure the final pH of supernatant.
7. Decant the supernatant from each jar and filter through a 0.2-µm Teflon membrane filter. The 0.2-µm filter is specified here rather than a 0.45-µm filter (a more traditional definition for dissolved metals) to simulate micro-filtration and obtain estimates of the best practical metals removal.
8. Collect filtrate samples and analyze for (dissolved) cadmium, lead, and zinc. Collect three separate aliquots of "treated effluent" in separate sample bottles. One of the aliquots will be analyzed in-house by CH2M HILL; the second will be archived for possible ultra-low level metals analysis by an outside lab, as appropriate; and the third will be archived for possible analysis by a CLP program lab, coordinated by EPA. This split sample collection procedure will be followed for all tests performed.

The results of Test Series 1 will be used to make a preliminary determination of the optimum pH for iron co-precipitation. The optimum pH will be used in Test Series 2.

TABLE 3-2
Iron Co-Precipitation pH Optimization

Jar Number	pH	Iron Dose [mg Fe/L][a]
F1.1	11.0	10.0
F1.2	10.5	10.0
F1.3	10.0	10.0
F1.4 (test duplicate)	10.0	10.0
F1.5	9.5	10.0
F1.6	9.0	10.0
F1.7 (test duplicate)	9.0	10.0
F1.8	8.0	10.0
F1.9 (test duplicate)	8.0	10.0
F1.10	7.0	10.0
F1.11 (method blank)[b]	No adjustment	None

[a] This arbitrarily selected dose will be increased if a strong floc does not form.
[b] Method blank is run with Milli-Q water instead of test water.

Test Series 2—Dose optimization

1. Add 1 liter of test water to each of nine beakers numbered as shown in Table 3-3 and add 1 liter of Milli-Q water to the tenth beaker (method blank). Place on jar stirrers and record starting pH and ORP.
2. Add iron stock solution to jars F3.1 to F3.9 to produce the doses indicated in Table 3-3, while rapid mixing at 100 rpm. Record the pH after iron addition and reagent volume added.
3. Add lime slurry or sulfuric acid solution to the jars to produce the optimum pH determined in Test Series 1. Make sure the pH levels stabilize. Record the volume of pH-adjustment reagent added to each jar.
4. Rapid mix for 1.5 minutes.
5. Slow mix at 15 to 20 rpm for 20 minutes. Adjust the paddle speed, if necessary, to promote flocculation and prevent floc sheer.
6. Turn off mixer and remove paddles from jars; allow samples to settle for 30 minutes. A longer settling time is acceptable if it facilitates filtration. Record observations on floc and settling characteristics and sludge quantity. Measure the final pH of supernatant.
7. Decant supernatant from each jar and filter through a 0.2-μm Teflon membrane filter. The 0.2-μm filter is specified here rather than a 0.45-μm filter (a more traditional definition for dissolved metals) to simulate micro-filtration and obtain estimates of the best practical metals removal.
8. Collect filtrate samples and analyze for (dissolved) cadmium, lead, and zinc. Collect three separate aliquots of "treated effluent" in separate sample bottles. One of the aliquots will be analyzed in-house by CH2M HILL; the second will be archived for possible ultra-low level metals analysis by an outside lab, as appropriate; and the third will be archived for possible analysis by a CLP program lab, coordinated by EPA.

The results of Test Series 2 will be used to make a preliminary determination of the optimum iron dose for metals removal by iron co-precipitation. The residual dissolved metals concentrations in the optimum dose and pH sample will be compared to the treatment goals to evaluate the potential effectiveness of iron co-precipitation.

3.3 Sulfide Precipitation Testing

This testing will evaluate the effectiveness of soluble metals removal from HDS process effluent by sulfide precipitation. In the sulfide precipitation process, dissolved metals are precipitated as sulfides, which, for most heavy metals, are more insoluble than the analogous hydroxides. Thus, sulfide precipitation theoretically can effect metals removal to lower residual concentrations. Sulfide can be added as a soluble compound such as sodium sulfide (Na_2S) or sodium hydrosulfide (NaHS), or as an insoluble compound such as ferrous sulfide (FeS). The insoluble process precludes the potential of H_2S emissions that can result from overdosing in the soluble sulfide process. The insoluble sulfide process may also avoid the pinfloc problem often associated with the soluble process. The insoluble sulfide process using FeS will be used in proof-of-principle Phase 1 testing. The same test water as used in iron co-precipitation testing will be used for sulfide precipitation testing: effluent from the HDS process thickener or pH-adjusted HDS effluent, based on the Subsection 3.1 test results.

TABLE 3-3
Iron Co-Precipitation Dose Optimization

Jar Number	pH	Iron Dose [mg Fe/L][a]
F2.1	Selected from Test Series 1	1.0
F2.2	Selected from Test Series 1	2.5
F2.3	Selected from Test Series 1	5.0
F2.4 (test duplicate)	Selected from Test Series 1	5.0
F2.5	Selected from Test Series 1	10
F2.6 (test duplicate)	Selected from Test Series 1	10
F2.7	Selected from Test Series 1	25
F2.8 (test duplicate)	Selected from Test Series 1	25
F2.9	Selected from Test Series 1	50
F2.10 (method blank)[b]	No adjustment	None

[a] Doses may be modified based on the results of Test Series 1.
[b] Method blank is run with Milli-Q water instead of test water.

3.3.1 Equipment and Supplies

The required equipment and supplies are the same as in iron co-precipitation testing.

3.3.2 Reagents

- Ferrous sulfide slurry—approximately 100 mg S/mL. Stock solution makeup: add 17.5 grams of reagent grade NaHS and 95.4 grams of reagent grade $FeSO_4$ to 100 mL of Milli-Q water. Stir slurry continuously on magnetic stirrer during use. This solution will be prepared freshly immediately prior to use.
- Lime slurry—approximately 10 mg/mL. Stock solution makeup: add 10 g reagent grade $Ca(OH)_2$ to 1 liter of Milli-Q water. Stir slurry continuously on magnetic stirrer during use. Make up a new batch of lime slurry each day of testing.
- Sulfuric acid solution for pH adjustment—6 N. Stock solution makeup: add 167 mL of reagent grade concentrated H_2SO_4 to a 1-liter volumetric flask and bring to volume with Milli-Q water.

Stock solution concentrations may be varied, as needed, to allow convenient pH adjustment.

3.3.3 Procedure

Standard jar test procedures will be used to optimize pH. Dose optimization is not necessary for Phase 1 testing because a large excess of FeS is used in the insoluble sulfide process. The jar test procedure is described below.

Test Series 3—pH optimization

1. Add 1 liter of test water to each of nine beakers numbered as shown in Table 3-4 and add 1 liter of Milli-Q water to the tenth beaker (method blank). Place beakers on jar stirrers and record starting pH and ORP.

2. Add ferrous sulfide slurry to jars S5.1 -S5.9 to produce a concentration of 500 mg S/L, while rapid mixing at 100 rpm. This concentration represents an inventory of FeS in the sample jar, similar to full-scale systems. A portion of the FeS will dissociate, and the sulfide ion will react with other metallic cations present in the sample. In the insoluble sulfide process, the dose does not affect metals removal as long as there is a sufficient excess of reagent available. Record the pH after FeS addition and reagent volume added.

3. Add lime slurry or sulfuric acid solution to the jars to produce the pH levels indicated in Table 3-4. Make sure the pH levels stabilize. Record the volume of pH-adjustment reagent added to each jar.

4. Rapid mix for 1.5 minutes.

5. Slow mix at 15-20 rpm for 20 minutes. Adjust paddle speed, if necessary, to promote flocculation and prevent floc sheer.

6. Turn off mixer and remove paddles from jars; allow samples to settle for 30 minutes (a longer settling time is acceptable if it facilitates filtration). Record observations on floc and settling characteristics and sludge quantity. Measure the final pH of supernatant.

7. Decant supernatant from each jar and filter through a 0.2-μm Teflon membrane filter. The 0.2-μm filter is specified here rather than a 0.45-μm filter (a more traditional definition for dissolved metals) to simulate micro-filtration and obtain estimates of the best practical metals removal.

8. Collect filtrate samples and analyze for (dissolved) cadmium, lead, and zinc. Collect three separate aliquots of "treated effluent" in separate sample bottles. One of the aliquots will be analyzed in-house by CH2M HILL; the second will be archived for possible ultra-low level metals analysis by an outside lab, as appropriate; and the third will be archived for possible analysis by a CLP program lab, coordinated by EPA.

The results of Test Series 3 will be used to make a preliminary determination of the optimum pH for metals removal by the insoluble sulfide precipitation process. The residual dissolved metals concentrations in the optimum pH sample will be compared to the treatment goals to evaluate the potential effectiveness of sulfide precipitation.

3.4 Sulfide Functional Ion Exchange Testing

This testing will evaluate the effectiveness of soluble metals removal from HDS process effluent by sulfide functional ion exchange. Ion exchange resins function by exchanging metal ions from solution for similarly charged ions attached to the immobile solid phase resin beads Phase 1 testing will involve batch testing of two types of sulfide functional ion exchange resins: Thiol and Thiouronium (thiourea based).

TABLE 3-4
Sulfide Precipitation pH Optimization

Jar Number	pH	FeS dose [mg S/L]
S3.1	10.0	500
S3.2 (test duplicate)	10.0	500
S3.3	9.5	500
S3.4	9.0	500
S3.5 (test duplicate)	9.0	500
S3.6	8.5	500
S3.7	8.0	500
S3.8 (test duplicate)	8.0	500
S3.9	7.0	500
S3.10 (method blank)*	No Adjustment	None

* Method blank is run with Milli-Q water instead of test water.

The reason for testing two resins is to evaluate the relative effectiveness and regenerability, as well as resin integrity. The Thiol resins have the potential to oxidize and also could produce a low pH effluent, such as pH 2 to 3, requiring upward readjustment. The Thiouronium-based resins are more oxidant tolerant but may be less selective for the target metals.

Two different types of tests are planned for Phase 1. During Phase 1a, batch isotherm testing will be conducted to estimate isotherm equation parameters and exchange capacity, and to evaluate the degree of treatment achievable under equilibrium conditions. During Phase 1b, iterative regeneration tests will be performed using the resins samples loaded in Phase 1a to obtain a preliminary indication of capacity and regenerability. The details of ion exchange testing are outlined below.

3.4.1 Equipment and Supplies

Equipment and supplies for ion exchange testing include: a shaker table, specialty-cleaned polyethylene bottles, vacuum filtering apparatus and a supply of 0.2- and 0.45-μm Teflon membrane filters, balance, magnetic stirrer with heating element and stirbars, specialty pre-cleaned and pre-analyzed polyethylene or polypropylene sample bottles, high-purity lab water supply (Milli-Q water), samples of virgin ion exchange resins, and standard lab glassware. All plasticware and glassware (other than the pre-cleaned sample bottles) will be thoroughly cleaned (acid washed, Milli-Q water rinsed) prior to use.

Reagents

- 10 percent hydrochloric acid solution (HCl) – approximtely 10.48 grams HCl/liter. Use 36.4 percent Optima-grade HCl solution. Add 12.17 ml of stock solution to a 500-mL volumetric flask half full of Milli-Q water. Bring to volume with Milli-Q water.
- Ion exchange resins – A minimum of one Thiol resin and one Thiouronium (thiourea based) resin will be tested. Table 3-5 shows potential resins and supplier information. A minimum of 250 grams of each resin type will be obtained to conduct the tests.

TABLE 3-5
Sulfide Functional Ion Exchange Resins

Resin Type	Model	Manufacturer
Thiol	T 100	Dianex Branford, Ontario 519/759-1603
Thiol	IONAC SR 4	Sybron Chemical Corporation Birmingham, NJ 609/893-1100
Thiol	IMAC TMR	Armac Chicago, IL 312/786-0400
Thiol	Duolite GT 73	Rohm and Haas Philadelphia, PA 215/592-3000
Thiouronium	IONAC SR 3	Sybron Chemical Corporation Birmingham, NJ 609/893-1100
Thiouronium	S 920	Purolite Bala Cynwyd, PA 800/343-1500

3.4.2 Batch Isotherm Test Procedure (Ion Exchange Testing Phase 1a)

1. Filter approximately 13 liters of test water through a 0.45-µm filter.
2. Measure the pH of filtered test water. If the pH is higher than 8.5, reduce to 8.0 to 8.5 using the 10 percent HCl solution. If the pH is lower than 6.0, raise to 6.0 to 6.5 using the calcium hydroxide slurry.
3. Collect a sample of the filtered test water and analyze for TAL metals (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn), pH, alkalinity, sulfate, and TDS.
4. Add 1 liter of neutralized test water or Milli-Q water to each of twelve bottles as shown in Table 3-6.
5. Measure and add Thiol resin to Bottles X1.1 through X1.6 at quantities shown in Table 3-6. Measure and add Thiouronium resin to Bottles X2.1 through X2.6 at quantities shown in Table 3-6.
6. Cap bottles, place on shaker table, and shake at moderate speed for 60 minutes.
7. Turn off shaker table and allow samples to settle for 5 minutes. Measure and record the pH of each treated water sample.
8. Decant treated water carefully so that no resin is present in the sample. Filter decanted water through a 0.2-µm Teflon membrane filter, and analyze the filtrates for TAL metals. Collect three sample aliquots from each test in separate sample bottles, as in

TABLE 3-6
Ion Exchange Resin Isotherm Testing Conditions

Bottle No.	Test Solution	Resin Type	Resin Dose*
X1.1	Prepared test water	Thiol	1 g
X1.2	Prepared test water	Thiol	2 g
X1.3	Prepared test water	Thiol	4 g
X1.4 (Duplicate)	Prepared test water	Thiol	4 g
X1.5	Prepared test water	Thiol	8 g
X1.6 (Method Blank)	Milli-Q water	Thiol	8 g
X2.1	Prepared test water	Thiouronium	1 g
X2.2	Prepared test water	Thiouronium	2 g
X2.3	Prepared test water	Thiouronium	4 g
X2.4 (Duplicate)	Prepared test water	Thiouronium	4 g
X2.5	Prepared test water	Thiouronium	8 g
X2.6 (Method Blank)	Milli-Q water	Thiouronium	8 g

* Dosages selected based on achieving theoretical exchange site saturation at a resin dose of 3 grams per 1 liter sample. Adjust dosages and sample size as needed after verifying resin data and test water characterization.

precipitation testing. Analyze one sample and archive the other two for possible low-level metals analysis and possible analysis by a CLP program lab.3.4.3 Loading/Regeneration Test Procedure (Ion Exchange Testing Phase 1b)

The ion exchange resin samples from four of the tests conducted in Phase 1a will be put through progressively more rigorous regeneration procedures to evaluate regenerability. Some information about the selectivity of the resins for one metal over another may also be found. The following procedure will be used.

1. Use the bottles containing the highest and lowest resin doses, of each type of resin, reserved from Phase 1 (for example, Bottle Nos. X1.1, X1.5, X2.1, X2.5).
2. Taking care not to lose any resin, rinse each resin sample and bottle from Phase 1a several times with Milli-Q water. During rinsing steps, transfer each resin sample to a smaller (100- to 125-mL polyethylene bottle). Discard the rinse water.
3. Add 40 mL of 10 percent HCl solution to each resin bottle at room temperature. Cap and shake for 1 hour on shaker table.
4. Remove regenerant solution and analyze for TAL metals. Archive a portion of the sample volume for possible low-level metals analysis by an outside lab. Develop mass balance.

5. If all the mass of the target metals removed by the resin in Phase 1a is accounted for in the regenerant solution (±10 percent), regeneration is considered to be completely successful. Discontinue further regeneration testing. If not, proceed to next step.
6. Taking care not to lose any resin, rinse the resin and bottle several times with Milli-Q water. Discard rinse water.
7. Add 40 mL of 10 percent HCl solution to each resin bottle and heat contents to 60 degrees Celsius. Cover and shake for 1 hour on shaker table.
8. Remove regenerant solution while still warm and analyze for TAL metals. Archive a portion of the sample volume for possible low-level metals analysis by an outside lab. Develop mass balance.
9. If all remaining mass of the target metals is accounted for in the regenerant solution (±10 percent), regeneration is considered to be complete. Discontinue further regeneration testing. If not, continue with next step.
10. Taking care not to lose any resin, rinse the resin and bottle several times with Milli-Q water. Discard rinse water.
11. Add 40 mL of concentrated (36.4 percent) HCl solution to each resin bottle. Cover and shake for 1 hour on shaker table at room temperature.
12. Remove regenerant solution and analyze for TAL metals. Archive a portion of the sample volume for possible low-level metals analysis by an outside lab. Develop mass balance.
13. If all remaining mass of the target metals is accounted for in the regenerant solution (±10 percent), regeneration is considered to be complete. Discontinue further regeneration testing. If not, proceed to next step.
14. Taking care not to lose any resin, rinse the resin and bottle several times with Milli-Q water. Discard rinse water.
15. Prepare chloride-saturated HCl solution by adding 300 mL of 36.4 percent HCl solution to 100 grams of $CaCl_2$ powder in bottle. Cover and shake for 30 minutes. Add more $CaCl_2$ powder to beaker if all previous powder dissolved and shake for an additional 15 minutes. Stop shaking and allow phase separation to occur. Decant supernatant and use as chloride-rich regenerant solution.
16. Add 20 mL of chloride-rich regenerant solution to each resin bottle. Cover and shake for 1 hour on shaker table at room temperature.
17. Remove regenerant solution and analyze for TAL metals. Archive a portion of the sample volume for possible low-level metals analysis by an outside lab. Develop mass balance.

SECTION 4
Sampling and Analysis

4.1 Sampling

Table 4-1 shows the field samples to be collected at the Bunker Hill Mine site. If feasible, all samples will be transferred to the sample containers using a peristaltic pump with clean Tygon tubing. Filtered samples will be collected by means of the peristaltic pump with an in-line cartridge filter. Before each sample is collected, a new filter will be inserted into the cartridge and the cartridge housing will be thoroughly rinsed with the waste to be collected. It is also advisable to collect samples in order from "cleanest" to "dirtiest" – that is, in reverse order from that shown in the table. The filter blank can be obtained in the lab using the same sampling apparatus used in the field. The sample cubitainers will be pre-cleaned in the lab before sampling, but the drum should be thoroughly rinsed with CTP effluent before sample collection. The CTP effluent field samples should be collected from the drum to be comparable to the lab CTP effluent (as-received) analyses.

All samples will be shipped by overnight courier to the Corvallis lab:

CH2M HILL
2300 N.W. Walnut Blvd
Corvallis, OR 97330
Attn: Kathy McKinley
Ph: 541/752-4271
Fax: 541/752-0276

Table 4-2 summarizes both lab and field samples to be collected during this study, analyses for each sample, and the data use of each test.

4.2 Analysis

Table 4-3 lists analytes, analytical sample requirements, preservation methods and holding times for samples generated in this study. In general, samples will be analyzed for metals by CH2M HILL using ICP or GFAA. Replicate samples will be archived, and selected samples will be analyzed by an outside lab using ICP/MS when very low-level measurements are required. Selected archived samples may also be analyzed by a CLP program lab, as coordinated by EPA. Analytical methods, procedures, and requirements are described in more detail in Section 5.

TABLE 4-1
Field Sampling Instructions

Waste	Sample Description	Sample Use
Raw AMD (field)	1-liter cubitainer preserved with HNO_3 (Spectra Grade) to pH < 2	Total TAL metals analysis
	1-liter cubitainer field filtered through a 0.45-μm filter then preserved with HNO_3 (Spectra Grade) to pH < 2	Dissolved TAL metals analysis
	1-gallon cubitainer, unpreserved	For analysis of SO4, TSS, TDS, lime demand, and solids formed
		Measure pH and temperature in the field
CTP influent (field)	1-liter cubitainer preserved with HNO_3 (Spectra Grade) to pH < 2	Total TAL metals analysis
	1-liter cubitainer field filtered through a 0.45-μm filter then preserved with HNO_3 (Spectra Grade) to pH < 2	Dissolved TAL metals analysis
	1-gallon cubitainer, unpreserved but shipped on ice	For analysis of SO4, TSS, TDS, lime demand, and solids formed
		Measure pH and temperature in the field
CTP effluent (field)	1-liter cubitainer preserved with HNO_3 (Spectra Grade) to pH < 2	Total Cd, Pb, Zn, Fe, Mn analysis
	1-liter cubitainer, unpreserved but shipped on ice	TSS
	1-liter cubitainer field filtered through a 0.45-μm filter then preserved with HNO_3 (Spectra Grade) to pH < 2	Dissolved Cd, Pb, Zn, Fe, Mn analysis
	N/A	Measure pH and temperature in the field
Filter blank (Milli-Q water)	1-liter cubitainer preserved with HNO_3 (Spectra Grade) to pH < 2	Asses metals contributed by filters/apparatus
CTP effluent	30-gallon polyethyene drum, unpreserved	Lab characterization and treatability testing

TABLE 4-2
Sampling and Analysis Plan

Sample ID	Sample Description	Analytes	Data Use
		Wastewater Characterization	
BH-AMD1-date	Raw AMD (field)	TAL metals (total and dissolved), pH, sulfate, TSS, TDS, lime demand and solids formed	Raw waste sample characterization
BH-Inf1-date	CTP influent (field)	TAL metals (total and dissolved), pH, sulfate, TSS, TDS, lime demand and solids formed	Treatment plant influent sample characterization
BH-Eff0-date	CTP effluent (field)	Cd, Pb, Zn, Fe, and Mn (total and dissolved), and pH	Field sample characterization
BH-FFB-date	Field filter blank (Milli-Q water)	Cd, Pb, Zn, Fe, and Mn (total and dissolved)	Assess metals contributed by field filter/apparatus
BH-Eff1-date	CTP effluent	TAL metals (total and dissolved), pH, alkalinity, sulfate, TSS, and TDS	As-received lab sample characterization
BH-P1.1-date BH-P1.5-date	pH-adjusted CTP influent	Cd, Pb, Zn, Fe, and Mn (dissolved)	Assess improvement in HDS performance at various pH levels
		Iron Co-Precipitation	
BH-Ferric-date	Ferric sulfate stock solution	Cd, Pb, Zn (dissolved)	Reagent blank
BH-Lime-date	Lime slurry stock solution	Cd, Pb, Zn (dissolved)	Reagent blank
BH-Sulfuric-date	Sulfuric acid stock solution	Cd, Pb, Zn (dissolved)	Reagent blank
BH-LFB1-date, BH-LFB2-date	Lab filter blanks (Milli-Q water)	Cd, Pb, Zn (dissolved)	Assess metals contributed by lab filters/apparatus
BH-F1.1-date BH-F1.11-date	Jar Test Series 1 effluents	Cd, Pb, Zn (dissolved)	Iron co-precipitation pH optimization
BH-F2.0-date	Untreated test water	Cd, Pb, Zn (dissolved)	Baseline re-analysis
BH-F2.1-date BH-F2.10-date	Jar Test Series 2 effluents	Cd, Pb, Zn (dissolved)	Iron co-precipitation dose optimization
		Sulfide Precipitation	
BH-Sulfide-date	Ferrous sulfide slurry	Cd, Pb, Zn (dissolved)	Reagent blank
BH-S3.0-date	Untreated test water	Cd, Pb, Zn (dissolved)	Baseline re-analysis
BH-S3.1-date BH-S3.10-date	Jar Test Series 3 effluents	Cd, Pb, Zn (dissolved)	Sulfide precipitation pH optimization

TABLE 4-2
Sampling and Analysis Plan

Sample ID	Sample Description	Analytes	Data Use
	Sulfide Functional Ion Exchange—Phase 1a Isotherm Testing		
BH-X1.0-date	Untreated test water	TAL metals (dissolved)	Baseline re-analysis
BH-X1.1-date BH-X1.6-date	Thiol resin effluents	TAL metals (dissolved)	Thiol resin metals removal results
BH-X2.1-date BH-X2.6-date	Thiouronium resin effluents	TAL metals (dissolved)	Thiouronium resin metals removal results
	Sulfide Functional Ion Exchange—Phase 1b Regeneration Testing		
BH-X1.1.1-date BH-X1.5.1-date BH-X2.1.1-date BH-X2.5.1-date	10% HCl regeneration solutions	TAL metals (dissolved)	Assess regeneration completeness
BH-X1.1.2-date BH-X1.5.2-date BH-X2.1.2-date BH-X2.5.2-date	Heated 10% HCl regeneration solutions	TAL metals (dissolved)	Assess regeneration completeness
BH-X1.1.3-date BH-X1.5.3-date BH-X2.1.3-date BH-X2.5.3-date	Concentrated (36.4%) HCl regeneration solutions	TAL metals (dissolved)	Assess regeneration completeness
BH-X1.1.4-date BH-X1.5.4-date BH-X2.1.4-date BH-X2.5.4-date	Chloride-rich concentrated (36.4%) HCl regeneration solutions	TAL metals (dissolved)	Assess regeneration completeness

TABLE 4-3
Sample Containers and Preservation Requirements

Matrix	Analysis	Collected Volume	Laboratory Required Volume	Preservation	Holding Time
Water	Total TAL Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn	1 liter polypropylene; Teflon-lined cap	1 liter polypropylene; Teflon-lined cap	pH <2 with HNO_3	6 months (mercury 28 days)
Water	Dissolved TAL Metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn	1 liter polypropylene; Teflon-lined cap	1 liter polypropylene; Teflon-lined cap	Filter via 0.45 micron, pH <2 with HNO_3	6 months (mercury 28 days)
Water	Sulfate	1 liter polypropylene; Teflon-lined cap	100 mL polypropylene or glass	Cool, 4°C	28 days
Water	TSS	The 1-liter volume collected for sulfate will also be sufficient for lime demand and TSS	300 mL polypropylene	Cool, 4°C	7 days
Water	Lime demand/ solids formed	The 1-liter volume collected for sulfate will also be sufficient for lime demand and TSS	250 mL polypropylene	Cool, 4°C	NA
Water	Alkalinity	1 liter polypropylene; Teflon-lined cap	1 liter	Cool, 4°C	14 days

4.3 Testing Quality Assurance (QA)

Special testing QA procedures that will be followed in this study are largely designed to avoid or account for contamination of samples by external (non-waste related) sources of metals. These are required because of the Draft TMDL based treatment goals (Table 1-1). Testing QA will include the following.

- Nitric acid used for sample presentation will be Spectra Grade.
- Hydrochloric acid used for ion exchange testing will be Spectra Grade.

- Sulfuric acid used for pH adjustment and jar testing will be Spectra Grade.
- All other reagents will be reagent grade.
- Specialty pre-cleaned and pre-analyzed sample bottles will be used for all treatability "effluent" samples.
- Test beakers, bottles, and other lab equipment will be thoroughly cleaned by acid washing (soaking in 10 percent "Baker Analyzed" HNO_3 for at least several hours, followed by a triple rinse with Milli-Q water) prior to use.
- A dedicated sampling system (pump and tubing) will be used for sample transfer.
- No metal equipment will be used in contact with the wastewater.
- The jar stirrer will be fitted with polyethylene or Teflon paddles, which will be acid washed between uses.
- Treatability testing will be performed in a clean room hood.
- Project lab staff will wear clean gowns, gloves, etc. when conducting tests or transferring samples.
- Stock solutions will be made up or used on a batch basis. Stock solutions that are not time sensitive will be kept separate from working solutions. Working solutions will be transferred to a separate container from the stock solution and used for a single testing batch; the remaining working solution will be discarded at the end of the test series.
- Milli-Q water method blanks will be carried through each step of the test series and analyzed.
- Filter blanks and reagent blanks will be collected and analyzed.
- Sample filters will be Teflon.
- Duplicate tests will be performed during each test series.

4.4 Field Quality Control Samples

4.4.1 Field Duplicate Samples

The field duplicate is an independent sample collected as close as possible to the original sample from the same source and is used to document sampling and analytical precision. Field duplicates will be collected at a minimum frequency of one per sampling event for each type of analysis.

4.4.2 Field Blank Samples

One field blank sample will be taken when the test waters are collected and analyzed for total and dissolved Cd, Pb, Zn, Fe, and Mn. Each field blank will be prepared by pouring blank water directly into the sample containers, or through the filter apparatus for filtered samples. Milli-Q water provided by the laboratory will be used for the samples. Field blanks will be prepared and labeled in the same manner as the field samples and sent "blind" to the laboratory.

4.4.3 Laboratory QC Sample

For each sampling event, one laboratory QC sample per analytical method will be collected. Laboratory QC samples will be collected and preserved in accordance with the sampling procedures described in Table 4-3. Each laboratory QC sample will be twice the normal sample volume.

4.5 Disposal of Materials

Disposable sampling materials will consist of filters, disposable gloves, paper towels, and miscellaneous paper waste. These will be considered non-regulated and will be disposed of in the trash. Unused sample liquids and residual liquids from laboratory treatability testing will be analyzed for metals during the course of this study. Measured metals concentrations will be compared to threshold levels in CH2M HILL's Laboratory Waste Management Plan to determine if they are dischargeable. Liquids determined to be dischargeable will be poured down the drain; liquids determined to be not dischargeable will be containerized, shipped back to the Bunker Hill site, and returned to the influent to the wastewater treatment plant.

4.6 Sampling Equipment Decontamination

Decontamination of sampling equipment will not be necessary because only disposable sampling equipment will be used.

4.7 Sample Containers

Sample containers will be obtained from the laboratories. All containers will be new and quality control checked by the supplier. The containers to be used for the specific analysis are shown in Table 4-3.

4.8 Sample Preservation

Sample containers will be shipped with the appropriate preservation shown in Table 4-3.

4.9 Sample Designations

The sample designations shown in Table 4-2 will be used.

4.10 Sample Packaging and Transport

The following procedures will be followed to ensure that the samples are intact when they arrive at the laboratory.

4.10.1 Packaging in the Field

Sample Containers

1. Place a custody seal over each sample container.

Preparing the Sample Cooler

1. Remove all previous labels used on cooler.
2. Seal all drain plugs with tape (outside and inside).
3. Place a cushioning layer of styrofoam popcorn at bottom of cooler (about 1-inch thick).
4. Line cooler with large plastic bag to contain samples.
5. Double bag all ice in plastic bags and seal. DO NOT USE THE BAG IN WHICH THE ICE WAS ORIGINALLY CONTAINED.

Packing Samples in Coolers

1. Place chain-of-custody form in ziplock bag and tape to the underside of the lid.
2. Place samples in upright position in cooler.
3. Fill void space between samples with styrofoam popcorn.
4. Place ice on top of samples and between samples.
5. Custody seal large plastic bag containing samples and packing material.

Closing of Cooler

1. Tape cooler lid with strapping tape, encircling cooler several times.
2. Place chain-of-custody seals on four sides of lid (suggest two seals in front, one in back, and one on a side).
3. Place "This Side Up" arrows on sides of cooler.

4.10.2 Transport

Place the cooler upright on a flat, stable surface to avoid tipping and/or sliding during transport. Keep out of the sun entirely. Transport to the laboratory (or an overnight courier for shipment to the contracted laboratory) immediately upon completion of sample collection. Intermediate stops should be avoided, with the exception of emergencies, in which case the situation should be noted in the field notebooks. If the samples are shipped via overnight courier, notify the laboratory that the samples are being shipped.

4.11 Field Documentation

4.11.1 Field Notebooks

All sampling activities will be recorded in a bound field notebook. Entries must be dated, legible, written in permanent ink, and contain accurate and inclusive documentation of project activities. Language should be objective and factual. Entries must include the following (if applicable):

- Names of all personnel
- Signature(s) of person(s) making log entries

- General description of weather conditions
- Location of each sampling point
- Flow/measurements: (Kellogg Tunnel flume and treatment plant effluent flume)
- Field measurements: pH, temperature, conductivity
- Date and time of sample collection
- Observations of sampling procedure
- Type of blank collected and method of collection
- Reference to photographs taken, if applicable
- Field observations and description of problems encountered or changes made to the original plan
- Duplicate sample location
- Legible corrections, which will be single lines through the error, signed and dated by the person making the correction
- Field instruments calibration information
- Name, address, and telephone number of the contracted analytical laboratory

4.12 Sample Paperwork

Samples will be sent to three labs as appropriate per procedures described in this plan: CH2M HILL's lab in Corvallis, Oregon; CAS Analytical in Redding, California for lime demand/solids formed testing; and another lab yet to be selected for EPA Method 6020 analyses.

4.12.1 Chain of Custody Paperwork

CH2M HILL chain-of-custody forms will be filled out for all samples collected. A chain-of-custody form will be completed for each sampling event; the laboratory copy will be delivered with the cooler, and the sampling team leader will retain the duplicate copy. All chain-of-custody forms and custody seals will be signed and dated by the sampling team member completing them.

4.12.2 Sample Labels

Each sample container will be labeled with a sample number, date of collection, type of analysis, and preservatives using water insoluble ink. Sample designations for each sampling event and location are described above.

SECTION 5

Quality Assurance and Control

5.1 Data Quality Objectives and Criteria for Measurement Data

The quality assurance (QA) objective of this plan is to develop implementation procedures that will provide data of known and appropriate quality for the needs identified in the previous sections and the data quality objectives identified in Tables 5-1 and 5-2 below; these data quality objects were prepared per EPA Data Quality Objectives (DQO) guidance (EPA, 1994).

Data quality is assessed by representativeness, comparability, accuracy, precision, and completeness. Definitions of these terms, the applicable procedures, and level of effort are provided below. The applicable QC procedures, quantitative target limits, and level of effort for assessing data quality are dictated by the intended use of the data and the nature of the analytical methods. Analytical parameters and applicable detection levels, analytical precision, accuracy, and completeness in alignment with needs identified in Tables 5-1 and 5-2 are presented in Table 5-3.

Detection limits shown in Table 5-3 are per DQO requirements identified in Tables 5-1 and 5-2. However, actual laboratory reporting limits may be higher due to sample specific matrix interferences or instrument limitations for ICP/MS. The sample-specific detection limits will be reported for the individual analytes.

Representativeness is a measure of how closely the results reflect the actual concentration or distribution of the chemical compounds in the matrix samples. Sampling plan design, sampling techniques, and sample handling protocols (for example, for storage, preservation, and transportation) have been developed and are discussed in previous sections of this document. The proposed documentation will establish that protocols have been followed and sample identification and integrity assured.

Comparability expresses the confidence with which one data set can be compared to another. Data comparability will be maintained using defined procedures and the use of consistent methods and consistent units. Actual detection limits will depend on the sample matrix and will be reported as defined for the specific samples.

TABLE 5-1
DQO Summary
Acid Mine Drainage (AMD) Treatability Testing – Phase 1
Bunker Hill Mine

Treatment Technology	Step 1 – Statement of Problem	Step 2 – Decision Question	Step 3 – Input to Decisions	Step 4 – Study Boundaries	Step 5 – Decision Rules	Step 6 – Limits of Decision Error	Step 7 – Optimize the Sampling Design
Development and Analysis of Test Water	Will Phase 1 testing results be skewed by use of shipped effluent from the existing Central Treatment Plant (CTP) to the treatability test laboratory?	Does the test water proposed for this treatability test work exhibit similar characteristics to the test water in the field? Are there changes during shipment? Can results of primary treatment (hydroxide precipitation) be further optimized through using a different target pH?	1. Characterization of Untreated AMD 2. CharacterizatioOn of CTP Influent 3. CharacterizatioOn of CTP Effluent 4. Impact of pH Changes on Dissolved Metals	Samples must be taken in single timeframe (July 1999). Temporal changes in AMD nature cannot be evaluated.	If samples of AMD and CTP influent are similar in character (metals concentrations within +/- 20 percent), proceed. If sample of CTP effluent agrees with historical data (normal CTP operation), proceed with pH variability test. If lower or higher optimum pH test results in significantly (>20%) lower dissolved metals concentrations, proceed.	Judgment will be applied to sample results analysis to determine whether AMD character meets objectives of testing.	Phased approach being used. This phase (Phase 1) is "proof of principal" phase. Test solution verification and judgment made regarding representativeness before treatability testing begins. HDS optimization through parametric pH testing to select optimum pH before treatability testing begins.
Iron Co-precipitation	Should this technology be carried to further analysis?	To what level can this technology reduce dissolved cadmium, lead, and zinc?	1. Neutralization requirement 2. Iron requirement. 3. Dissolved metals concentration following treatment.	Variability of influent will not be evaluated in this phase.	If concentrations of dissolved cadmium, lead, and zinc are lower than the other technologies and/or approach the treatment goals, this technology will be considered for Phase 2 testing.	Judgment will be applied to analysis to determine whether this technology meets requirements for further consideration.	Phased approach being used. This phase (Phase 1) is "proof of principal" phase. Parametric pH testing to select optimum pH before variability is adding iron concentration is evaluated. Test duplicates used to assess variability in results
Insoluble Sulfide Precipitation	Should this technology be carried to further analysis?	To what level can this technology reduce dissolved cadmium, lead, and zinc?	1. Neutralization requirement 2. Dissolved metals concentration following treatment.	Variability of influent will not be evaluated in this phase.	If concentrations of dissolved cadmium, lead, and zinc are lower than the other technologies and/or approach the treatment goals, this technology will be considered for Phase 2 testing.	Judgment will be applied to analysis to determine whether this technology meets requirements for further consideration.	Phased approach being used. This phase (Phase 1) is "proof of principal" phase. Parametric pH testing to select optimum pH. Test duplicates used to assess variability in results. Optimization of sulfide dose deferred to Phase 2. Representative (and conservatively high) dose used in Phase 1.
Sulfide functional ion exchange.	Should this technology be carried to further analysis?	To what level can this technology reduce dissolved cadmium, lead, and zinc? What are major cost-related impacts of this technology?	1. Neutralization requirement (if any) 2. Dissolved metals concentration following treatment. 3. Regeneration requirement and effectiveness	Variability of influent will not be evaluated in this phase.	If concentrations of dissolved cadmium, lead, and zinc are lower than the other technologies and/or approach the treatment goals, and/or the cost impacts appear competitive, this technology will be considered for Phase 2 testing.	Judgment will be applied to analysis to determine whether this technology meets requirements for further consideration. For example, if this technology can produce substantially lower metals concentrations relative to the precipitation technologies, it may be promoted to Phase 2 even if costs are not competitive.	Phased approach being used. This phase (Phase 1) is "proof of principal" phase. Different resin loadings tested to evaluated resin requirement. Test duplicates used to assess variability in results. Sequenced and progressively more difficult regeneration schemes to be evaluated. Optimization deferred to phase 2

COPC = Chemical of potential concern
NFA = No further action
UXO = Unexploded ordnance
VOC = Volatile organic compound
SVOC = Semi-volatile organic compound
TPH = Total petroleum hydrocarbon
USFWS = United States Fish and Wildlife Service
PRGs = Preliminary Remediation Goals
EPRGs = Ecological Preliminary Remediation Goals

F/SI = Focused Site Inspection
SI = Site Inspection
AWQC = Ambient Water Quality Criteria
NWR = National Wildlife Refuge
DTSC = Department of Toxic Substances Control
bgs = below ground surface
CAD = cartridge actuated device
AA = Atomic Absorption
CSL = Close Support Laboratory

BTEX = benzene, toluene, ethylbenzene, and xylene
mg/kg = milligrams per kilogram
PAH = polycyclic aromatic hydrocarbon
mm = millimeter

TABLE 5-2
Data Needs and Uses

Parameter	Data Use	Data Users	Needed Detection Level
Lime Demand/Solids Formed	Assess strength of acid mine drainage (AMD) and determine quantity of lime required to treat a unit volume, and the mass of sludge solids formed per unit volume.	Regulators, geochemists, hydrogeologists, and process engineers	2 lb/1,000 gal
Alkalinity	Assess buffering capacity of treated AMD and determine quantity of acid required to treat a unit volume.	Regulators, geochemists, hydrogeologists, and process engineers	10 mg/L (as $CaCO_3$)
pH (Field and Lab)	Assess relative hydrogen ion concentration in AMD and help evaluate pH process control needs for treatment plant.	Regulators, geochemists, hydrogeologists, and process engineers	0.1 pH units
Sulfate	Sulfate is the major anion in the AMD. The sulfate concentration in raw AMD should be proportional to the cations and will be used as an indicator of AMD strength. The sulfate concentration will also be used to assess potential for gypsum scaling of treatment equipment and in mass/charge balance calculations.	Regulators, geochemists, hydrogeologists, and process engineers	100 mg/L
Temperature (Field)	Record sample temperature for future CTP design.	Regulators, geochemists, hydrogeologists, and process engineers	1 degree Celsius
TSS	Assess the potential sizing for solids filtration and/or processing equipment.	Regulators, geochemists, hydrogeologists, and process engineers	10/mg/L
Total TAL Metals (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn)	These are the major cations in the AMD. Zn, Pb, and Cd are the major metals of aquatic toxicity concern. These concentrations will be used to assess treatment requirements, treatment effectiveness, and regeneration efficiency.	Regulators, geochemists, hydrogeologists, and process engineers	For Method 6020: Cd and Hg 0.0001 mg/L; Pb 0.0003 mg/L; Zn 0.005 mg/L; Others 0.001 mg/L (except magnesium 5 mg/L)
Dissolved TAL Metals (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Ob, Sb, Se, Tl, V, Zn)	The dissolved concentrations of metals will be compared to the total concentrations. Dissolved metal is of primary concern for aquatic toxicity. It is expected that the totals and dissolved concentrations will be similar except when there is high TSS. This data will help evaluate this assumption.	Regulators, geochemists, hydrogeologists, and process engineers	Same as above

TABLE 5-3
Criteria for Measurement Data

Parameter	Method	Target Detection Limit	Accuracy (% Recovery)	Precision (Relative % Deviation)	Completeness (%)
Total and Dissolved Metals					
Zn	SW6010, 7000 series, 6020[a]	5 μg/L[a]	75-125	±25	90
Cd	SW6010, 7000 series, 6020[a]	0.1 μg/L[a]	75-125	±25	90
Hg	SW7470A	0.1 μg/L[a]	75-125	±25	90
Pb	SW6010, 7000 series, 6020[a]	0.3 μg/L[a]	75-125	±25	90
Mg	SW6010, 7000 series, 6020[a]	5000 μg/L	75-125	±25	90
Other TAL Metals[f]	SW6010, 7000 series, 6020[a]	1 μg/L	75-125	±25	90
Sulfate	EPA 300 or 375[b]	10 mg/L	75-125	±25	90
Alkalinity	EPA 310[b]	10 mg/L as $CaCo_3$	75-125	±25	90
TSS[d]	EPA 160-2[b]	5 mg/L	75-125	±25	90
Lime Demand/ Solids Formed	c	2 lb/l000 gal	75-125	±25	90
pH	Field[e]	NA	NA	±0.1 pH units	90
Temperature	Field[e]	NA	NA	± 1°C	90

[a] EPA Test Methods for Evaluating Solid Waste, 3rd Edition and Updates. The listed detection limits are for Method 6020, analysis prior to Method 6020 final analyses will be carried out as described in the previous section per ICP or graphite furnace. Target detection limits for these preliminary analyses will be per standard method detection limits.

[b] EPA 600/4-79-020 *Methods for Chemical Analysis of Water and Wastes*, revised March 1983.

[c] Procedures are provided in CH2M HILL's Bunker Hill Mine Water Management Project Quality Assurance Project Plan, October 1998.

[d] Total suspended solids.

[e] Per field instrument manual procedure.

[f] TAL metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn

NA Not applicable.

Accuracy is an assessment of the closeness of the measured value to the true value. For samples, accuracy of chemical test results is assessed by spiking samples with known standards and establishing the average recovery. For a matrix spike, known amounts of a standard compound identical to the compounds being measured are added to the sample. A quantitative definition of average recovery accuracy is given in Section 5.11. Accuracy measurement will be carried out with a minimum frequency of 1 in 20 samples analyzed.

Precision of the data is a measure of the data spread when more than one measurement has been taken on the same sample. Precision can be expressed as the relative percent difference; a quantitative definition is given in Section 5.11. The level of effort for precision measurements will be a minimum of 1 in 20 samples.

Completeness is a measure of the amount of valid data obtained from the analytical measurement system and the complete implementation of defined field procedures. The quantitative definition of completeness is given in Section 5.11. The target completeness objective will be 90 percent; the actual completeness may vary depending on the intrinsic nature of the samples. The completeness of the data will be assessed during QC reviews.

5.2 Special Training Requirements/Certification

All project staff working on the site must follow requirements specified in the project's Health and Safety Plan (HSP). The HSP describes the specialized training required for personnel on this project and the documentation and tracking of this training.

5.3 Documentation and Records

Laboratory data documentation will be per laboratory-specific standard operating procedures and methods/quality control procedures specified in Sections 5.4. Field documentation will be as described in Section 4.0. Overall project documentation will be per RACS Program quality assurance plan.

5.4 Quality Control Requirements

Field Quality Control Procedures

Field quality control requirement will be as described in Section 4.0.

Laboratory Quality Control Procedures

Metals analyses will be subject to the following:

- Methodology as specified in Table 5.3 and strategy described in Section 4.2
- Calibrations and internal QC checks as shown in Tables 5-4 (for 6010 ICP), 5-5 (for graphite furnace 7000 series), 5-6 (for 6020 ICP/MS), and 5-7 (for Hg, 7470)
- Accuracy and precision criteria per Table 5-3
- Blanks per Tables 5-4 through 5-6
- Documentation will be equivalent to EPA Contract Laboratory Program (CLP) QA/QC full data package.

Analyses other than metals will be subject to methods specified in Table 5-3 and quality control requirements specified in Table 5-8 and the following are minimum quality control requirements where applicable:

- Minimum three-point initial calibration—subject to relative standard deviation or coefficient of variation criteria
- Daily continuing calibrations—subject to relative percent difference or deviation criteria
- Daily laboratory control standards measurements—subject to laboratory-specific limits not to exceed recovery limits of 75 to 125 percent
- Accuracy and precision measurements at a frequency of 5 percent
- Blank measurement at a frequency of 5 percent
- Documentation equivalent to EPA CLP QA/QC full data package

TABLE 5-4
Calibration and QC Requirements for SW6010A (ICP)

QC Check	Frequency*	Criteria	Corrective Action
Initial calibration (a blank and at least one standard)	Before initial sample analysis, every 24 hours, whenever modifications are made to the analytical system, or when continuing calibration verification fails	N/A	N/A
Initial calibration verification (ICV); must be from second source	Immediately following each initial calibration	All analytes within ±10% of expected value	Correct problem and repeat initial calibration.
Calibration blank	After every calibration verification (ICV and CCV)	No analytes detected at or above the CRDL	Correct the problem, then reanalyze previous 10 samples.
Continuing calibration verification (CCV)	After every analytical batch or at the conclusion of each analytical day, whichever is more frequent	All analytes within ±10% of expected value	Recalibrate and reanalyze all samples since the last acceptable CCV
Method Blank	At least one per analytical batch	No analytes detected at or above the CRDL	Correct the problem and re-prep and reanalyze all associated samples
Interference check standard (ICS)	At the start and end of each analytical batch	All analytes within ±20% of expected value	Correct the problem, recalibrate, and reanalyze ICS and all affected samples.
MS/MSD	One set per 20 samples	All analytes within limits specified in Table 5-3 (75%-125%)	None
LCS	At least one per analytical batch	All analytes within limits specified in Table 5-3 (75%-125%)	Correct the problem, and re-prep and reanalyze the LCS and all samples in the analytical batch.
Dilution test	Each new sample matrix	Result from 1:5 dilution must be within ±10% of the undiluted sample result (applies only if undiluted sample result is at least 25 times the MDL)	Perform post-digestion spike addition.
Post-digestion spike addition	When dilution test fails	Recovery within 75-125% of expected value	Flag data.

*Analytical Batch: defined as a group of Bunker Hill treatability samples, not to exceed 20, analyzed using identical instrumental settings using the same lot of analytical reagents and working solutions which are performed by the same analyst.

TABLE 5-5
Calibration and QC Requirements for Metals by Graphite Furnace (7000 series)

QC Check	Frequency*	Criteria	Corrective Action
Multi-point initial calibration (a blank and at least three standards)	Before initial sample analysis, every 24 hours, whenever modifications are made to the analytical system, or when continuing calibration verification fails	Correlation coefficient of linear regression is ≥ 0.995	Correct the problem and repeat the initial calibration.
Initial calibration verification (ICV); must be from second source	Immediately following each initial calibration	All analytes within ±10% of expected value	Correct the problem and repeat initial calibration.
Calibration blank	After every calibration verification (ICV and CCV)	No analytes detected at or above the CRDL	Correct the problem, then reanalyze previous 10 samples.
Continuing calibration verification (CCV)	After every analytical batch or at the conclusion of each analytical day, whichever is more frequent	All analytes within ±10% of expected value	Recalibrate and reanalyze all samples since the last acceptable CCV
Method Blank	At least one per analytical batch	No analytes detected at or above the CRDL	Correct the problem and re-prep and reanalyze all associated samples
MS/MSD	One set per 20 samples	All analytes within limits specified in Table 5-3 (75%-125%)	None
LCS	At least one per analytical batch	All analytes within limits specified in Table 5-3 (75%-125%)	Correct the problem, and re-prep and reanalyze the LCS and all samples in the analytical batch.
Dilution test	Each new sample matrix	Result from 1:5 dilution must be within ±10% of the undiluted sample result (applies only if undiluted sample result is at least 25 times the MDL)	Perform post-digestion spike addition.
Recovery test	When dilution test fails	Recovery within 85-115% of expected value	Analyze all samples by MSA

*Analytical Batch: defined as a group of Bunker Hill treatability samples, not to exceed 20, analyzed using identical instrumental settings using the same lot of analytical reagents and working solutions which are performed by the same analyst.

TABLE 5-6
Summary of Calibration and QC Procedures for Method SW6020

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
SW6020	TAL Metals	MS tuning sample	Prior to initial calibration and calibration verification	RSD ≤5% for all analytes	Retune instrument then reanalyze tuning solution
		Initial multipoint calibration (minimum 3 standards and a blank)	Daily initial calibration prior to sample analysis	Correlation coefficient ≥0.995 for linear regression	Correct problem then repeat initial calibration
		Calibration blank	Before beginning a sample run, after every 10 samples and at end of the analysis sequence	No analytes detected ≥ RL	Correct problem then analyze calibration blank and previous 10 samples
		Continuing calibration verification (Instrument Check Standard)	Before beginning a sample run, after every 10 samples and at the end of the analysis sequence	All analyte(s) within ±10% of expected value	Correct problem then repeat calibration and reanalyze all samples since last successful calibration
		Demonstrate ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample	Once per analyst	QC acceptance criteria, Table 5-3	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria
		Method blank	One per analytical batch	No analytes detected ≥ RL	Correct problem reprep and analyze method blank and all samples processed with the contami-nated blank
		Interference check solution (ICS)	At the beginning and end of an analytical run or twice during an 12 hour period, whichever is more frequent	Within ±20% of expected value	Terminate analysis; locate and correct problem; reanalyze ICS; reanalyze all affected samples

TABLE 5-6
Summary of Calibration and QC Procedures for Method SW6020

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action[a]
SW6020	TAL Metals	LCS for the analyte	One LCS per analytical batch	QC acceptance criteria, Table 5-3	Correct problem reprep and analyze the LCS and all samples in the affected analytical batch
		Dilution test	Each new sample matrix	1:4 dilution must agree within ±10% of the original determination	Perform post digestion spike addition
		Post digestion spike addition	When dilution test fails	Recovery within 75-125% of expected results	Dilute the sample; reanalyze post digestion spike addition
		MS/MSD	One MS/MSD per every 20 samples per matrix	QC acceptance criteria, Table 5-3	none
		Internal Standards (ISs)	Every sample	IS intensity within 30-120% of intensity of the IS in the initial calibration	Perform corrective action as described in method SW6020, section 8.3
		MDL study	Yearly	Detection limits established shall be < the RLs in Table 5-3	none

TABLE 5-7
Calibration and QC Requirements for Mercury (SW7470/SW7471/CLP)

QC Check	Frequency*	Criteria	Corrective Action
Multi-point initial calibration (a blank and at least five standards)	Before initial sample analysis, every 24 hours, whenever modifications are made to the analytical system, or when continuing calibration verification fails	Correlation coefficient of linear regression is ≥ 0.995	Correct the problem and repeat the initial calibration.
Initial calibration verification (ICV); must be from second source	Immediately following each initial calibration	All analytes within ±20% of expected value	Correct the problem and repeat initial calibration.
Calibration blank	After every calibration verification (ICV and CCV)	No analytes detected at or above the reporting limit	Correct the problem, then reanalyze previous 10 samples.
Continuing calibration verification (CCV)	After every 10 samples and at the end of the analysis sequence	All analytes within ±20% of expected value	Recalibrate and reanalyze all samples since the last acceptable CCV
Method Blank	At least one per analytical batch	No analytes detected at or above the CRDL	Correct the problem and re-prep and reanalyze all associated samples
MS/MSD	One set per 20 samples	75-125%	None
LCS	At least one per analytical batch	75-125%	Correct the problem, and re-prep and reanalyze the LCS and all samples in the analytical batch.
Dilution test	Each new sample matrix	Result from 1:5 dilution must be within ±10% of the undiluted sample result (applies only if undiluted sample result is at least 25 times the MDL)	Perform post-digestion spike addition.
CRDL standard	Once per analytical batch	Report recovery	
Recovery test	When dilution test fails	Recovery within 85-115% of expected value	Analyze all samples by MSA

* Analytical batch: defined as a group of treatability samples, not to exceed 20, analyzed using identical instrumental settings using the same lot of analytical reagensts and working solutions which are performed by the same analyst.

TABLE 5-8
Calibration and QC Requirements for General Inorganic Chemistry

QC Check	Frequency*	Criteria	Corrective Action
Multi-point initial calibration (minimum three points); for titrimetric methods, titrant must be standardized in duplicate, and the average concentration used; for gravimetric methods, balance must be calibrated using standard weights that bracket sample weights.	Prior to sample analysis, or when calibration verification fails	Correlation coefficient for linear regression must be ≥ 0.995 (not applicable to titrimetric and gravimetric methods)	Correct the problem and repeat the initial calibration.
Continuing calibration verification (CCV) – does not apply to titrimetric and gravimetric methods.	At the start of each analytical batch and at the conclusion of each analytical day	All analytes within ±10% of expected value	Correct the problem, then recalibrate and reanalyze all samples since the last acceptable CCV.
Method Blank	At least one per analytical batch	No analytes detected at or above the CRDL	Correct the problem and re-prep and reanalyze all associated samples
MS/MSD (One MS and one set of laboratory duplicates may be substituted for MS/MSD)	One set per 20 samples	Within limits specified in Table 5-3 (75%-125%)	None
LCS	At least one per analytical batch	Within limits specified in Table 5-3 (75%-125%)	Correct the problem, and re-prep and reanalyze the LCS and all samples in the analytical batch.

*Analytical Batch: defined as a group of Bunker Hill treatability samples, not to exceed 20, analyzed using identical instrumental settings using the same lot of analytical reagents and working solutions which are performed by the same analyst.

5.5 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Field Equipment

Field equipment, will be inspected and maintained by CH2M HILL (contractor) on a routine basis. Prior to using any instrument in the field, it will be calibrated in accordance with the manufacturer's instructions and field-tested. If applicable records of inspection, calibration and field testing will be maintained in the daily field diary.

Analytical Laboratory Equipment

Laboratory analysis equipment is routinely tested, inspected, and maintained in accordance with the laboratory-specific QA/QC manual and the manufacturer's requirements. Records of equipment maintenance, calibration and testing are maintained by the laboratory.

5.6 Instrument Calibration and Frequency

All field instruments and equipment used during this project will be operated, calibrated, and maintained according to the manufacturers' guidelines and recommendations. Operation, calibration, and maintenance will be performed by personnel who have been properly trained in these procedures. A routine schedule and record of instrument calibration and maintenance will be maintained throughout the duration of this project.

Calibration of laboratory owned and operated equipment will be in accordance with the laboratory quality assurance/quality control plan, the methods and the quality control specified in Sections 5.4.

5.7 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables anticipated for use at the site primarily include sample containers and sample collection equipment. Consumables will be purchased in original packaging and stored in a manner that protects their usability.

5.8 Data Acquisition Requirements (Non-Direct Measurements)

Data may be entered into an electronic spreadsheet and/or database that will be subject to the data management practices described below. Laboratory hard copy deliverables will be per specification in Section 5.4.

5.9 Data Management

Data management can be defined as comprising the functions of creating and accessing stored data, enforcing data storage conventions, and regulating data input and output. The stored data will include parameters measured in soils at the site.

For this project, data management will involve the use of a computerized data management system. The system will provide a centralized, secure location for data of known quality that can be shared and used for multiple purposes. The data management system will assist in the information flow for the project by providing a means of cataloging, organizing, archiving, and accessing information.

The data management system will include three main elements:

The database: An organized and structured storehouse of data used for multiple purposes. Initially a spreadsheet program will be used, and if justified by project needs a relational database will be used latter.

Data management procedures: The steps involved in the data management process

Personnel: The project staff who develop, implement, and administer the database and procedures

These elements are briefly described in the following subsections.

The Database

A spreadsheet will be created to store data collected as part of this effort. The software being used in support of the spreadsheet is Microsoft Excel. If justified by project needs, Microsoft Access will be the relational database.

Data Management Procedures

Data management procedures are a crucial part of the data management system. Established procedures are necessary to ensure consistency among data sets, internal database integrity, and a verified, usable data set. The tasks and procedures that will be performed for all project data before they are entered include:

- **Data mapping.** The process by which the collected environmental data are selected, marked, and corrected named for entry into the database.
- **Electronic data interchange.** To facilitate data interchange between the analytical laboratory and the data user. Detailed specifications will be developed for both receipt and delivery of electronic data including data importing and data exporting.
- **Data entry and verification.** The process by which data are correctly entered into the database including data preparation, data import and entry, and data verification.
- **Data presentation and analysis.** Data from the database may be presented in two types of reports: 1) Appendix-style reports which (tabular listings sorted by station and sample ID); and 2) Summary statistics (frequency of detection, mean, minimum values,

maximum values, standard deviation, and variance) sorted by station, depth and parameter.

- **Data administration.** Effective administration of the data management system will reduce the likelihood of errors and ensure the integrity of the database. Data administration tasks include: data redundancy control, operation and maintenance of the database, documentation of the data management process, and closing out the data management task in both interim and final stages of completion.

Personnel

Successful implementation of a data management system requires a clear definition of responsibilities. The data management system will be carried out by project staff. Responsibilities includes database integrity, redundancy control, data sharing and version control, performance, security, and backup. The staff have a comprehensive understanding of the database structure, software, and associated analysis tools. Responsibilities include data logging and tracking, data preparation, data entry and verification, data archiving, data requests, and report generation.

5.10 Data Assessment and Response Actions

Data Assessments

The system audit is a systematic check of a qualitative nature consisting of an onsite review of a laboratory's quality assurance system and physical facilities for sampling, calibration, and measurement. System audits for this project will be performed on an as-needed basis.

Performance audits provide a systematic check of laboratory operations and measurement systems by comparing independently obtained data with routinely obtained data. Performance audits will be scheduled on an as-needed basis.

Reports to Management—Response Actions

If the quality control audit results in detection of unacceptable conditions or data, the SM will be responsible for developing and initiating corrective action. Onsite staff will be notified if the nonconformance relates to their work. Corrective action may include:

- Reanalyzing the samples
- Resampling and analyzing
- Evaluating and amending sampling and analytical procedures
- Accepting data, acknowledging level of uncertainty or inaccuracy by flagging the data

5.11 Data Validation and Usability

Data Review, Validation, and Verification Requirements

All data for all parameters will undergo two levels of review and validation: 1) at the laboratory; and 2) outside the laboratory by chemists independent of the laboratory.

Validation and Verification Methods

Initial data reduction, validation, and reporting at the laboratory will be carried out as described in the laboratory standard operating procedures.

Independent data validation by EPA or their designee will follow EPA Contract Laboratory Program National Guidelines for Inorganic Data Review, February 1994, if applicable.

Reconciliation with Data Quality Objectives

Assessment of data for precision, accuracy, and completeness will be per the following quantitative definitions.

Precision

If calculated from duplicate measurements:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2) / 2}$$

RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = larger of the two observed values

If calculated from three or more replicates, use relative standard (RSD) rather than RPD:

$$RSD = (s / \bar{y}) \times 100\%$$

RPD = relative standard deviation
s = standard deviation
$\bar{y}$ = mean of replicate analyses

Standard deviation, s, is defined as follows:

$$S = \sqrt{\sum_{i=1}^{n} \frac{(yi/y)^{-2}}{n-1}}$$

s = standard deviation
y_i = measured value of the i^{th} replicate
$\bar{y}$ = mean of replicate analyses
n = number of replicates

Accuracy

For measurements where matrix spikes are used:

$$\%R = 100\% \times \left[\frac{S - U}{C_{sa}}\right]$$

%R	=	percent recovery
S	=	measured concentration in spiked aliquot
U	=	measured concentration in unspiked aliquot
C_{sa}	=	actual concentration of spike added

For situations where a standard reference material (SRM) is used instead of or in addition to matrix spikes:

$$\%R = 100\% \times \left[\frac{C_m}{C_{sm}}\right]$$

%R	=	percent recovery
C_m	=	measured concentration of SRM
C_{sm}	=	actual concentration of SRM

Completeness (Statistical)

Defined as follows for all measurements:

$$\%C = 100\% \times \left[\frac{V}{T}\right]$$

%C	=	percent completeness
V	=	number of measurements judged valid
T	=	total number of measurements

5.12 References for Section 5

U.S. Environmental Protection Agency. 1998. *EPA Guidance for Quality Assurance Project Plans,* EPA QA/G5, EPA/600/R-98/018, February.

U.S. Environmental Protection Agency. 1994a. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review,* February.

U.S. Environmental Protection Agency. 1994b. *Guidance for the Data Quality Objectives Process,* EPA QA/G4, September.

SECTION 6

Data Recording and Reporting

Data collected during this treatability study will consist of test set-up data and measurements, lab observations, and analytical data and will be managed in accordance with procedures described in Section 5.9. Test data and observations will be recorded in a dedicated lab notebook and on lab forms developed for this project. Analytical data will be tabulated in computer spreadsheets. Data summaries also will be generated in tabular and graphical formats. Hard copies of raw data and/or summarized data will be attached to the project reports.

SECTION 7

Data Analysis and Interpretation

7.1 Wastewater Characterization

Raw AMD and CTP influent samples collected synoptically with the CTP effluent samples will be characterized to link treatability effectiveness and residual metals concentrations after treatment with mine drainage characteristics. CTP effluent field and as-received lab characterization data will be compared to evaluate changes during shipping.

The "best" pH for HDS system operation will be determined, for the purposes of this study, by comparing concentrations of dissolved cadmium, lead, and zinc in the actual HDS effluent sample to concentrations in the pH-adjusted HDS effluent samples. The sample containing the lowest dissolved metals concentrations may be selected for use as test water in subsequent treatability testing.

7.2 Iron Co-Precipitation and Sulfide Precipitation Testing

Two decision points occur during the precipitation studies, which require selection of optimum treatment conditions:

- Selection of the optimum operating pH (Test Series 1 and 3).
- Selection of the optimum iron dose (Test Series 2).

These selections will be made based on the conditions that result in the minimum dissolved concentrations of cadmium, lead, and zinc after treatment. The potential effectiveness of each treatment method will ultimately be determined by comparing the concentrations of dissolved metals achieved with the optimum pH/dose treatment conditions to the treatment goals. Based on these results, recommendations will be developed regarding whether the precipitation treatment processes will be retained for more detailed testing in Phase 2.

The results of the chemical precipitation jar tests will be presented in tables and/or as figures of metals concentrations versus treatment condition values (pH or dose). Since the reagents will be added as solutions, the volume of reagent added will be recorded and the results will account for dilution impacts.

7.3 Sulfide Functional Ion Exchange

The ion exchange isotherm data will be evaluated according to a commonly used isotherm model such as the Freundlich equation (shown below) to determine isotherm constants.

$$\frac{x}{m} = KC_e^{1/n}$$

Where:

x = mass of solute adsorbed (removed from solution)
m = mass of adsorbent or resin
C_e = equilibrium concentration of solute in liquid
K and 1/n = empirical constants characteristic of the system.

Knowing these constants K and 1/n, the removal capacity per unit mass of resin (x/m) can be predicted for a given equilibrium effluent concentration, C_e. The equilibrium capacities can then be compared for different resin types.

The regeneration testing results will be evaluated using a mass balance approach to assess the completeness of regeneration achieved by the different regeneration solutions tested.

SECTION 8
Health and Safety

AMD, CTP influent, and CTP effluent sampling will be conducted in accordance with CH2M HILL's Bunker Hill Mine Water Monitoring Project Health and Safety Plan.

Treatability testing will be conducted in accordance with CH2M HILL's comprehensive laboratory health and safety plan.

SECTION 9

Residuals Management

Residuals generated during this treatability testing will consist of unused AMD, CTP influent, CTP effluent samples, and treated effluent from laboratory testing. All of these samples will be analyzed for metals during the course of the study, and measured concentrations will be compared to threshold levels in CH2M HILL's Laboratory Waste Management Plan to determine if they are dischargeable. Residuals determined to be dischargeable will be poured down the drain; residuals determined to be not dischargeable will be containerized and shipped back to the Bunker Hill Mine site, where they will be returned to the influent to the treatment plant.

SECTION 10

Reports

The methods, results, and conclusions of the Phase 1 work will be reported in a Treatability Testing Report. The report will provide a discussion of the testing results with respect to the test objectives listed in Section 2. Recommendations for Phase 2 testing will also be given.

SECTION 11

Schedule

It is anticipated that the work will begin during July 1999. The Phase 1 treatability testing should take approximately 4 to 6 weeks after receipt of the wastewater samples at the laboratory, assuming analytical turnaround times of less than 2 weeks can be obtained. The Draft Treatability Testing Report will be prepared within 30 days after receipt of all analytical data. Phase 2 testing design is anticipated to occur concurrently with preparation of the Phase 1 report.

SECTION 12

Staffing

As CH2M HILL's overall project manager for the Bunker Hill Mine Water activities, Jim Stefanoff will have overall responsibility for technical and financial performance of this task. As task leader, Bob York, an industrial wastewater engineer with 22 years of experience who has evaluated the AMD treatment system at Bunker Hill since 1995, will coordinate the treatability study and prepare the report. Jim Mavis and Gary Hickman will be senior advisers on this work. The test work will be preformed by staff of CH2M HILL's Applied Sciences Treatability Testing Laboratory in Corvallis, Oregon, under the supervision of Dr. Hickman.